

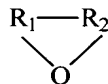
What is Claimed is:

1. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene oxide, carbon dioxide and an aliphatic monohydric alcohol comprising:

(a) reacting an alkylene oxide with carbon dioxide in the presence of a halogen-free carbonation catalyst at a temperature in the range of about 50°C to 250°C and at a pressure of at least about 1379 kPa (200 psi) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said catalyst; and

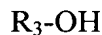
(b) reacting said cyclic carbonate with said aliphatic monohydric alcohol in the presence of said catalyst to provide a crude product stream comprising said dialkyl carbonate and said diol, wherein said crude product stream exhibits a halogen concentration of about 5 ppm or less.

2. The process of Claim 1, wherein said alkylene oxide is of the formula:



wherein R_1 and R_2 independently of one another denote a divalent group represented by the formula $-(CH_2)_m-$, wherein m is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group, wherein R_1 and R_2 can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:



wherein R_3 is an aliphatic C_1 - C_{12} hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group.

3. The process of Claim 1, wherein said halogen-free carbonation catalyst is selected from the group consisting of [1,1'(1-butylbenzimidazol-

2yl)pentane]copper(II) di(trifluoromethanesulfonate), and hydroxides, carbonates or bicarbonates of quaternary ammonium bases.

4. The process of Claim 1, wherein said halogen concentration is about 2 ppm or less.
5. The process of Claim 1, wherein said pressure is in the range of about 3448 kPa to 6897 kPa (500 to 1000 psig) and the temperature is in the range of about 150°C to 200°C.
6. The process of Claim 1, wherein the molar ratio of CO₂ to alkylene oxide is in the range from about 1.05 to 1.15 and the molar ratio of aliphatic monohydric alcohol to cyclic carbonate is in the range from about 2:1 to 6:1.
7. The process of Claim 1, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of up to 40% by weight, based upon total weight of said crude cyclic carbonate stream.
8. The process of Claim 7, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.
9. The process of Claim 1, wherein said aliphatic monohydric alcohol contains dialkyl carbonate in an amount of up to 40% by weight, based upon the total weight of said aliphatic monohydric alcohol and said dialkyl carbonate.
10. The process of Claim 1, further comprising a step of recovering said dialkyl carbonate and said diol from said crude product stream.
11. The process of Claim 1, further comprising:
 - (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;

- (ii) recycling said first recycle stream to transesterification step (b);
- (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said catalyst from said crude product stream; and
- (iv) recycling at least a portion of said second recycle stream to said carbonation step (a) and/or at least a portion of said second recycle stream to said transesterification step (b).

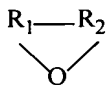
12. The process of Claim 2, wherein said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

13. The process of Claim 1, wherein said transesterification step (b) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reaction zones, a distillation column with a plurality of reaction zones having heat exchangers disposed between the distillation column and each reaction zone, and a distillation column with a plurality of reaction zones wherein bottoms thereof are optionally recycled to the distillation column.

14. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene oxide, carbon dioxide and an aliphatic monohydric alcohol comprising:

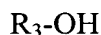
- (a) reacting an alkylene oxide with carbon dioxide in the presence of a halogen-free carbonation catalyst to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said catalyst; and
- (b) reacting said cyclic carbonate and said halogen-free carbonation catalyst with said aliphatic monohydric alcohol in the presence of a transesterification catalyst to provide a crude product stream comprising said dialkyl carbonate and said diol, wherein said crude product exhibits a halogen concentration of about 5 ppm or less.

15. The process of Claim 14, wherein said alkylene oxide is of the formula:



wherein R_1 and R_2 independently of one another denote a divalent group represented by the formula $-(CH_2)_m-$, wherein m is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of a C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group, wherein R_1 and R_2 can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:



wherein R_3 is an aliphatic C_1 - C_{12} hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group.

16. The process of Claim 14, wherein said halogen-free, carbonation catalyst is selected from the group consisting of [1,1'(1-butylbenzimidazol-2-yl)pentane]copper(II) di(trifluoromethanesulfonate), and hydroxides, carbonates or bicarbonates of quaternary ammonium bases.

17. The process of Claim 14, wherein said halogen concentration is about 2 ppm or less.

18. The process of Claim 14, wherein said transesterification catalyst is at least one catalyst selected from the group consisting of: anion exchange resins, inorganic metal oxides and inorganic solid support catalysts containing metals, and compounds or complexes of at least one element of groups 1, 2, 4-10, or 12-17 of the periodic table.

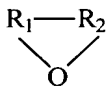
19. The process of Claim 14, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of from about 0.5 to 40% by weight, based upon the total weight of said crude cyclic carbonate stream.
20. The process of Claim 19, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.
21. The process of Claim 14, wherein said aliphatic monohydric alcohol further comprises dialkyl carbonate in an amount of up to 15% by weight, based upon the total weight of said aliphatic monohydric alcohol and said dialkyl carbonate.
22. The process of Claim 14, further comprising:
- (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;
 - (ii) recycling said first recycle stream to transesterification step (b);
 - (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said homogeneous carbonation catalyst from said crude product stream; and
 - (iv) recycling at least a portion of said second recycle stream to carbonation step (a) and at least a portion of said second recycle stream to said transesterification step (b).
23. The process of Claim 15, wherein said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.
24. The process of Claim 14, wherein said transesterification step (b) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reaction zones, a

distillation column with a plurality of reaction zones having heat exchangers disposed between the distillation column and each reaction zone, and a distillation column with a plurality of reaction zones wherein bottoms thereof are optionally recycled to the distillation column.

25. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene which comprises:

- (a) reacting said alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a halogen-free carbonation catalyst at a temperature in the range of about 50°C to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said catalyst; and
- (c) reacting said cyclic carbonate with an aliphatic monohydric alcohol in the presence of said catalyst to provide a crude product stream comprising said dialkyl carbonate and said diol, wherein said crude product stream exhibits a halogen concentration of about 5 ppm or less.

26. The process of claim 25, wherein said alkylene oxide is of the formula:



wherein R_1 and R_2 independently of one another denote a divalent group represented by the formula $-(CH_2)_m-$, wherein m is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group, wherein R_1 and R_2 can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:

$R_3\text{-OH}$

wherein R_3 is an aliphatic $C_1\text{-}C_{12}$ hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a $C_1\text{-}C_{10}$ alkyl group and a $C_6\text{-}C_{10}$ aryl group.

27. The process of Claim 25, wherein said halogen-free carbonation catalyst is selected from the group consisting of [1,1'-(1-butylbenzimidazol-2-yl)pentane]copper(II) di(trifluoromethanesulfonate), and hydroxides, carbonates or bicarbonates of quaternary ammonium bases.
28. The process of Claim 25, wherein said halogen concentration is about 2 ppm or less.
29. The process of Claim 25, wherein said pressure is in the range of about 3448 kPa to 6897 kPa (500 to 1000 psig) and the temperature is in the range of about 150°C to 200°C.
30. The process of Claim 25, wherein a molar ratio of said carbon dioxide to said alkylene oxide is in the range from about 1.05 to 1.10 and a molar ratio of said aliphatic monohydric alcohol to said cyclic carbonate is in the range from about 2:1 to 6:1.
31. The process of Claim 25, wherein said crude cyclic carbonate stream further comprises glycol impurities in an amount of up to 40% by weight, based upon total weight of said crude cyclic carbonate stream.
32. The process of Claim 31, wherein said cyclic carbonate is ethylene carbonate, said aliphatic monohydric alcohol is methanol, and said glycol impurities comprise ethylene glycol and higher molecular weight glycols.

33. The process of Claim 25, wherein said aliphatic monohydric alcohol contains said dialkyl carbonate in an amount of up to 40% by weight, based upon the total weight of said aliphatic monohydric alcohol and said dialkyl carbonate.

34. The process of Claim 25, further comprising the further step of recovering said dialkyl carbonate and said diol from said crude product stream.

35. The process of Claim 25, further comprising:

- (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;
- (ii) recycling said first recycle stream to the transesterification step (c);
- (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said catalyst from said crude product stream; and
- (iv) recycling at least a portion of said second recycle stream to carbonation step (b) and/or at least a portion of said second recycle stream to said transesterification step (c).

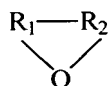
36. The process of Claim 26, wherein said alkylene is ethylene, said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

37. The process of Claim 25, wherein said transesterification step (c) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reactors, a distillation column with a plurality of reactors having heat exchangers disposed between the distillation column and each reactor, and a distillation column with a plurality of reactors wherein bottoms thereof are optionally recycled to the distillation column.

38. An integrated process for the production of a dialkyl carbonate and a diol from an alkylene which comprises:

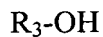
- (a) reacting at least a portion of said alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a halogen-free carbonation catalyst at a temperature in the range of about 50°C to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said carbonation catalyst; and
- (c) reacting said cyclic carbonate and said carbonation catalyst with an aliphatic monohydric alcohol in the presence of a transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol, wherein said crude product stream exhibits a halogen concentration of about 5 ppm or less.

39. The process of Claim 38, wherein said alkylene oxide is of the formula:



wherein R_1 and R_2 independently of one another denote a divalent group represented by the formula $-(\text{CH}_2)_m-$, wherein m is an integer from 1 to 3, which is unsubstituted or substituted with at least one substituent selected from the group consisting of a C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group, wherein R_1 and R_2 can share the same substituent; and

said aliphatic monohydric alcohol is of the formula:



wherein R_3 is an aliphatic C_1 - C_{12} hydrocarbon group which is unsubstituted or substituted with at least one substituent selected from the group consisting of a C_1 - C_{10} alkyl group and a C_6 - C_{10} aryl group.

40. The process of Claim 39, wherein said carbonation catalyst is selected from the group consisting of [1,1'-(1-butylbenzimidazol-2-yl)pentane]copper(II) di(trifluoromethanesulfonate), and hydroxides, carbonates or bicarbonates of quaternary ammonium bases.
41. The process of Claim 39, wherein said halogen concentration is about 2 ppm or less.
42. The process of Claim 39, wherein said transesterification catalyst is at least one catalyst selected from the group consisting of: anion-exchange resins, inorganic metal oxides and inorganic solid support catalysts containing metals, and compounds or complexes of at least one element of groups 1, 2, 4-10, or 12-17 of the periodic table.
43. The process of Claim 39, wherein said transesterification catalyst comprises a transitional alumina.
44. The process of Claim 39, further comprising:
- (i) separating a first recycle stream comprising unreacted aliphatic monohydric alcohol from said crude product stream;
 - (ii) recycling said first recycle stream to the transesterification step (c);
 - (iii) separating a second recycle stream comprising unreacted cyclic carbonate and said carbonation catalyst from said crude product stream; and
 - (iv) recycling at least a portion of said second recycle stream to the carbonation step (b) and at least a portion of said second recycle stream to said transesterification step (c).
45. The process of Claim 39, wherein said cyclic carbonate is ethylene carbonate and said aliphatic monohydric alcohol is methanol.

46. The process of Claim 39, wherein said transesterification step (c) occurs in a reaction vessel selected from the group consisting of: a reactive distillation column, a distillation column with at least a plurality of reactors, a distillation column with a plurality of reactors having heat exchangers disposed between the distillation column and each reactor, and a distillation column with a plurality of reactors wherein bottoms thereof are optionally recycled to the distillation column.

47. A process for producing polycarbonate which comprises the following steps:

- (a) reacting an alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a halogen-free carbonation catalyst at a temperature in the range of about 50°C to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said carbonation catalyst;
- (c) reacting said cyclic carbonate with an aliphatic monohydric alcohol in the presence of a transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol, wherein said crude product stream has a halogen concentration of about 5 ppm or less;
- (d) separating said dialkyl carbonate from said diol, thereby producing a dialkyl carbonate-enriched stream;
- (e) reacting said dialkyl carbonate-enriched stream and phenol in the presence of a metal-containing catalyst at a temperature in the range between about 80°C to 300°C and at a pressure in the range between about 2 kPa to 4000 kPa (absolute pressure), thereby producing diphenyl carbonate and alkanol;

- (f) separating said diphenyl carbonate from said alkanol, thereby producing a diphenyl carbonate-enriched stream;
- (g) reacting said diphenyl carbonate-enriched stream with bisphenol-A, thereby producing polycarbonate and phenol; and
- (h) separating said polycarbonate from said phenol, thereby producing a polycarbonate-enriched stream.

48. A process for producing polycarbonate which comprises the following steps:

- (a) reacting an alkylene with an oxygen-containing gas, thereby producing an alkylene oxide, carbon dioxide, and water;
- (b) reacting at least a portion of said alkylene oxide with said carbon dioxide in the presence of a halogen-free carbonation catalyst at a temperature in the range of about 50°C to 250°C and at a pressure of at least about 1379 kPa (200 psig) to provide a crude cyclic carbonate stream comprising a cyclic carbonate and said carbonation catalyst;
- (c) reacting said cyclic carbonate and said carbonation catalyst with an aliphatic monohydric alcohol in the presence of a transesterification catalyst to provide a crude product stream comprising a dialkyl carbonate and diol, wherein said crude product stream has a halogen concentration of about 5 ppm or less;
- (d) separating said dialkyl carbonate from said diol, thereby producing a dialkyl carbonate-enriched stream;
- (e) reacting said dialkyl carbonate-enriched stream and phenol in the presence of a metal-containing catalyst at a temperature in the range between about 80°C to 300°C and at a pressure in the range between about 2 kPa to 4000 kPa (absolute pressure), thereby producing diphenyl carbonate and alkanol;

- (f) separating said diphenyl carbonate from said alkanol, thereby producing a diphenyl carbonate-enriched stream;
- (g) reacting said diphenyl carbonate-enriched stream with bisphenol-A, thereby producing polycarbonate and phenol; and
- (h) separating said polycarbonate from said phenol, thereby producing a polycarbonate-enriched stream.